PATENT ABSTRACTS OF JAPAN

(11)Publication number : 10-110257

(43)Date of publication of application : 28.04.1998

(51)Int.Cl. C23C 14/06
A61L 15/16
C23C 14/48

(21)Application number : 08-262906

(22)Date of filing : 03.10.1996

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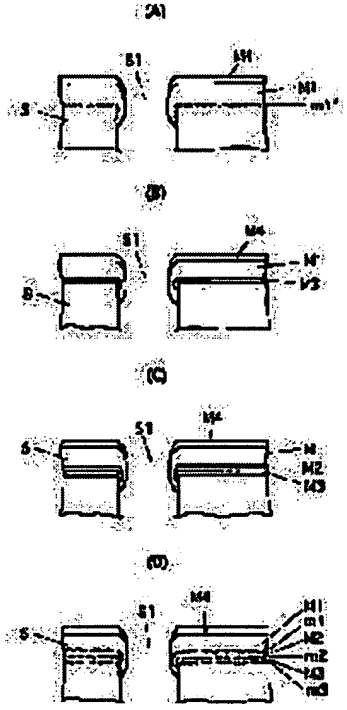
(54) COATING MATERIAL FOR MEDICAL USE

(57)Abstract:

PROBLEM TO BE SOLVED: To suppress proliferation of bactera at a wound part for a long time and to prevent adhesion of coating to the wound part by coating the side to be abutted with the skin in an air permeable porous substrate with metallic coating having antibacterial activity and forming diamond-like carbon (DLC) adhesion preventing coating on the outside in a state in which the antibacterial metallic coating is partially exposed.

SOLUTION: On the side of the face to be contacted with the skin in a non- woven fabric coating substrate S of a high polymer material, antibacterial coating M1 composed of at least one kind among Ag, Au, Pt, Cu, Sn and Ir is formed by an ion vapor deposition thin coating forming method, and furthermore, on the outside, DLC coating M4 is formed by a plasma CVD method. Their coating thickness is regulated to 0.5 to 5μm, and, between the antibacterial coating M1 and the substrate S, a mixed layer m1' of both is allowed to exist to increase their adhesion. In this coating material for medical use, since the antibacterial coating M1 covers slightly to the inside of an air hole S1 of the substrate S, and on the other hand, the DLC coating 4 on the outside is not formed to the inside of the hole S1, the antibacterial coating M1 is partially exposed, and its activity can be shown (fig. A).



LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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CLAIMS

[Claim(s)]
[Claim 1] The medical-application cladding material characterized by forming the antibacterial film which is from the metal which has antimicrobial activity on the field side where reliance is divided into the skin of a medical-application cladding material base, and forming the diamond-like carbon (DLC) film in the condition that this antibacterial film is partially exposed to the outside of this antibacterial film.
[Claim 2] The medical-application cladding material according to claim 1 formed by the ion vacuum evaporationo thin film forming method said antibacterial film uses vacuum evaporationo and ion irradiation together.
[Claim 3] The medical-application cladding material according to claim 1 or 2 with which said antibacterial film consists of at least one sort of matter among silver (Ag), gold (Au), platinum (Pt), copper (Cu), zinc (Zn), tin (Sn), and iridium (Ir).
[Claim 4] The medical-application cladding material according to claim 1, 2, or 3 said whose base is a permeability porosity base and whose thickness of said antibacterial film is 0.5 micrometers or more 5 micrometers or less.
[Claim 5] The medical-application cladding material according to claim 4 whose thickness of said DLC film is 0.05 micrometers or more 0.5 micrometers or less.
[Claim 6] A medical-application cladding material given in either of claims 1-5 in which said DLC film is formed by the plasma-CVD method.
[Claim 7] A medical-application cladding material given in either of claims 1-6 which are what the base of said medical-application cladding material becomes from polymeric materials.
[Claim 8] The adhesion layer which consists of at least one sort of matter chosen as the field side where reliance is divided into the skin of a medical-application cladding material base from titanium (Ti), chromium (Cr), and silicon (Si) is formed. On the outside of this adhesion layer, silver (Ag), gold (Au), platinum (Pt), copper (Cu), The medical-application cladding material characterized by having formed the antibacterial film which consists of at least one sort of matter chosen from zinc (Zn), tin (Sn), and iridium (Ir), and forming the diamond-like carbon (DLC) film in the condition that this antibacterial film is partially exposed to the outside of this adhesion layer.
[Claim 9] The medical-application cladding material according to claim 8 formed by the ion vacuum evaporationo thin film forming method at least one side uses vacuum evaporationo and ion irradiation together among said adhesion layer and said antibacterial film.
[Claim 10] The medical-application cladding material according to claim 8 or 9 said whose base is a permeability porosity base and whose thickness of said antibacterial film is 0.5 micrometers or more 5 micrometers or less.
[Claim 11] The medical-application cladding material according to claim 10 whose thickness of said DLC film is 0.05 micrometers or more 0.5 micrometers or less.
[Claim 12] A medical-application cladding material given in either of claims 8-11 in which said DLC film is formed by the plasma-CVD method.

[Claim 13] A medical-application cladding material given in either of claims 8-12 which are what the base of said medical-application cladding material becomes from polymeric materials.
[Claim 14] The adhesion layer which consists of at least one sort of matter chosen as the field side where reliance is divided into the skin of a medical-application cladding material base from titanium (Ti), chromium (Cr), and silicon (Si) is formed. The barrier layer which consists of gold (Au), platinum (Pt) or gold, and platinum is formed in the outside of this adhesion layer. On the outside of this barrier layer, silver (Ag), platinum (Pt), copper (Cu), zinc (Zn), The medical-application cladding material characterized by having formed the antibacterial film which consists of at least one sort of matter chosen from tin (Sn) and iridium (Ir), and forming the diamond-like carbon (DLC) film in the condition that this antibacterial film is partially exposed to the outside of this antibacterial film.
[Claim 15] The medical-application cladding material according to claim 14 formed by the ion vacuum evaporationo thin film forming method the film of [1 / at least] said adhesion layer, said barrier layer, and said antibacterial film (layer) uses vacuum evaporationo and ion irradiation together.
[Claim 16] The medical-application cladding material according to claim 14 or 15 said whose base is a permeability porosity base and whose thickness of said antibacterial film is 0.5 micrometers or more 5 micrometers or less.
[Claim 17] The medical-application cladding material according to claim 16 whose thickness of said DLC film is 0.05 micrometers or more 0.5 micrometers or less.
[Claim 18] A medical-application cladding material given in either of claims 14-17 in which said DLC film is formed by the plasma-CVD method.
[Claim 19] A medical-application cladding material given in either of claims 14-18 which are what the base of said medical-application cladding material becomes from polymeric materials.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the medical-application cladding material for protecting skin deficit parts, such as a medical-application cladding material especially the wound section, and the burn section.
[0002]
[Description of the Prior Art] The wound section of the skin, the burn section, etc. are usually covered with the medical-application cladding material (dry dressing material) for recovering by the incrustation, where this part is maintained at dryness, the medical-application cladding material (wet dressing material) for recovering by maintaining this part at a moderate damp or wet condition, and promoting the migration of an epidermal cell, etc., in order to protect this part. Although a desiccation necrosis of a wound is controlled and wet dressing material has prompt recovery, an exudate tends to collect between this wet dressing material and a wound side, and this part serves as an environment which bacteria etc. tend to increase.
[0003] About these medical-application cladding materials, in order to control growth of the bacteria in a wound side, to give the matter which has antimicrobial activity is tried. As antimicrobial activity matter given to a medical-application cladding material, an inorganic compound is used abundantly from a viewpoint of stability. For example, according to JP,64-15054,A, what included the zeolite which supported antibacterial metals, such as silver, copper, and zinc, in the front face or the whole of the medical-application cladding material which consists of silicone rubber is indicated.
[0004] Moreover, according to JP,4-90764,A and JP,4-272764,A, a hydrophilic polymer is chemically combined with one front face of the medical-application cladding material of the shape of film which consists of porosity polyolefine and a thermoplastic polyurethane elastomer, respectively, and the thing which made extent which does not thin-film-ize an antibacterial metal by vacuum evaporationo or ion beam exposure adhere to this polymer plane of union further is indicated, for example.
[0005] Moreover, in case a wound side is covered with a medical-application cladding material, applying the cream pharmaceuticals containing an antimicrobial agent to a wound side, and preventing infection is also performed.
[0006]
[Problem(s) to be Solved by the Invention] However, it is easy to produce adhesion with a wound side, and both the aforementioned dry dressing material and wet dressing material have the problem that it is accompanied by pain at the time of dressing material exchange. Moreover, the aforementioned antibacterial zeolite is not applied to the front face of a medical-application cladding material, or the property of a base material may deteriorate by spreading and distribution of an antibacterial zeolite, and, generally the medical-application cladding material included in the whole is seldom used.
[0007] Moreover, although the metal is given to extent which is not thin-film-ized in the medical-application cladding material to which vacuum evaporationo etc. carried out the aforementioned antibacterial metal in order to avoid exfoliation of the metal membrane by crookedness of a base

material, since sufficient adhesion with a base material is not acquired in addition but it is easy to produce exfoliation of a metal while in use, it is difficult to maintain sufficient antimicrobial activity over long duration. Moreover, by the approach of applying the cream pharmaceuticals containing an antimicrobial agent, these the greater part of cream pharmaceuticals will be absorbed by the medical-application cladding material, and it takes the time and effort which effectiveness is bad and applies.
[0008] Then, this invention makes it a technical problem to offer the medical-application cladding material which adhesion with a wound side cannot produce easily. Moreover, this activity can be maintained and used for it over a long time, and this invention makes it a technical problem to offer further the medical-application cladding material which adhesion with a wound side cannot produce easily while it has sufficient antimicrobial activity which can control growth of the bacteria in the wound section of the skin etc.
[0009]
[Means for Solving the Problem] The diamond-like carbon (DLC) film is formed in the condition that the antibacterial film which is from the metal which has antimicrobial activity on the field side where reliance is divided into the skin of the base of a medical-application cladding material is covered, and this antibacterial film exposes the medical-application cladding material of this invention to the outside of this antibacterial film partially.
[0010] The DLC film of the outermost layer is effective in adhesion control with a wound side. Although Ag which has strong antimicrobial activity typically can be mentioned as a metal which has said antimicrobial activity, noble metals, such as Au, Pt, and Ir, Cu, Zn, Sn, etc. can be used. Said antibacterial film can consist of at least one sort of matter among these.
[0011] As an ingredient of the medical-application cladding material base of this invention, synthetic macromolecule ingredients, such as naturally-ocurring-polymers ingredients, such as cotton usually used as an ingredient of a medical-application cladding material, polyethylene, and polyethylene terephthalate, etc. can be illustrated, and it is not limited especially. Moreover, the mode can illustrate the shape of the shape of a nonwoven fabric, and a film, the mode which piled up ******. The bases (for example, a nonwoven fabric, a film, etc. of permeability porosity which consist of polymeric materials) of the permeability porosity which consists of polymeric materials, such as cotton, polyethylene, and polyethylene terephthalate, as a typical thing can be mentioned.
[0012] It is desirable for a base to make thickness of said antibacterial film 0.5-micrometer or more 5-micrometer or less extent in the case of the base (for example, a porosity film and a nonwoven fabric base [from]) of permeability porosity. On the relation which forms the DLC film in the outermost layer, when this has thickness smaller than 0.5 micrometers the place where it is desirable for the antibacterial film to turn to the interior of a hole (opening) of not only the front face of a medical-application cladding material base but a base, it is difficult for it for the antibacterial film to turn to the interior of a hole (opening) of a base, and it is because there is a possibility that sufficient antimicrobial activity may not be obtained. Moreover, it is because it will be easy to produce a crack on the film and will become easy to produce exfoliation along with this crack, if larger than 5 micrometers. Moreover, thickness is said within the limits and is suitably defined according to the membranous quality of the material, the quality of the material of a medical-application cladding material base, the pore (opening) area of this base, etc. For example, it is possible to make thickness small at extent which permeability will worsen if an opening aspect product decreases remarkably by film formation to the inner skin of each opening, or an edge when choked up comparatively densely [when the opening aspect product of this base is small (i.e., a front face)], and does not decrease an opening aspect product remarkably since it is not desirable practically. Also for this reason, 5 micrometers or less are desirable.
[0013] As for the thickness of said DLC film, it is desirable to consider as 0.05-micrometer or more (for example, 0.1 micrometers or more) 0.5-micrometer or less extent. It is difficult for this to carry out film formation to homogeneity, if thickness is smaller than 0.05 micrometers, and it is because there is a possibility that the adhesion prevention effectiveness with sufficient wound side may not be acquired, and is because there is a possibility that the aforementioned antibacterial film may be extensively covered by the DLC film, and the antimicrobial activity of the antibacterial film may not fully be

demonstrated when larger than 0.5 micrometers.
[0014] Since the DLC film is formed in the surface part which touches the skin according to the medical-application cladding material of this invention, it is hard to adhere to a wound side, and the pain at the time of medical-application cladding material exchange becomes few things. Moreover, although the antibacterial film which becomes from the metal which has at least one sort of antimicrobial activity inside this DLC film is formed and this film is covered by the DLC film, since it has exposed partially For example, when adopting the aforementioned permeability porosity base, it can leave ****** which is not covered with the DLC film by forming this film to the interior of a hole (opening) of this base. Such an antibacterial film exposure part and the exudate from a wound side contact, the antibacterial metal in this film is eluted in an exudate as ion, and the antimicrobial activity which the antibacterial film has is fully demonstrated.
[0015] In the medical-application cladding material of this invention, it is possible to have the adhesion layer which consists of at least one sort of matter among Ti, Cr, and Si between said medical-application cladding material bases and said antibacterial film. For example, when the antibacterial film is Ag film, Ti adhesion layer can be adopted. Each of these adhesion layer ingredients has comparatively good adjustment with the both sides of the ingredient adopted as an ingredient of usual medical-application cladding materials, such as polymeric materials, and said antibacterial film ingredient, and the role which raises the adhesion of this base and the antibacterial film is carried out.
[0016] Furthermore, in the medical-application cladding material of this invention, it has the barrier layer which consists of Au, Pt, or these both between said adhesion layers and said antibacterial film, and it is possible that said antibacterial film consists of at least one sort of matter among Ag, Pt, Ir, Cu, Zn, and Sn. For example, the antibacterial film can adopt the barrier layer which consists of Pt when an adhesion layer is a Ti layer by Ag film. When it does not have a barrier layer, there is a possibility that oxygen may be spread through the antibacterial film, and this oxygen reaches the interface part of the antibacterial film and an adhesion layer in that case, and it becomes easy to produce exfoliation of the antibacterial film in this part. Moreover, although it is easy to diffuse an antibacterial film constituent into an adhesion layer and the antibacterial film becomes easy to exfoliate in that case when it does not have a barrier layer, a barrier layer can control diffusion of such oxygen or (reaching) an antibacterial film constituent, and can raise the adhesion of the antibacterial film.
[0017] When forming the direct antibacterial film on a base in the medical-application cladding material of this invention, without forming an aforementioned adhesion layer and an aforementioned barrier layer, this film formation When it has the antibacterial film and an adhesion layer and has the antibacterial film, a barrier layer, and an adhesion layer for film (layer) formation of either or both sides, it is possible to perform film (layer) formation of at least 1 by the ion vacuum evaporationo thin film forming method which uses vacuum evaporationo and ion irradiation together.
[0018] Thereby, in an operation of exposure ion, while an ion irradiation side is activated, these both mixolimnion is formed between the formed film (layer) and its lower layer, and the adhesion of this film (layer) improves. As exposure ion, nitrogen ion, a hydrogen ion, inactive gas ion (helium (helium) ion, neon (Ne) ion, argon (Ar) ion, krypton (Kr) ion, xenon (Xe) ion, etc.), etc. can be used.
[0019] Although the acceleration voltage at the time of ion irradiation changes with quality of the materials of an ion kind and an ion irradiation side etc., it is desirable to consider as V or more 1002-kV or less extent. This is because there is a possibility that the effectiveness of ion irradiation may become an ununiformity in an exposure side, and the field whose film adhesion is not enough may be generated if smaller than 100V, and is because possibility that degradation of a medical-application cladding material base will arise under the effect of the heat accompanying ion irradiation is large when larger than 2kV.
[0020] Moreover, in the medical-application cladding material of this invention, as a medical-application cladding material base, it is possible to use what cleaned the front face by ion irradiation before film (layer) formation, and film (layer) adhesion becomes what was further excellent in this case. Thus, the long duration use of the formation film (layer) can be carried out by adopting the ion vacuum evaporationo thin film forming method, becoming what cannot exfoliate easily from the conventional

film also by crookedness of a base, and maintaining antimicrobial activity, as for such a cladding material.

[0021] Moreover, in the medical-application cladding material of this invention, said DLC film can illustrate what was typically formed by the plasma-CVD method, although especially the formation approach is not limited. In addition, since the adhesion of said DLC film and film (layer) of the inside is also good, the medical-application cladding material of this invention is formed on the base as the whole film at adhesion fitness.

[0022]

[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained with reference to a drawing. Drawing 1 (A), (B), (C), and (D) are some expanded sectional views of the medical-application cladding material which is the operation gestalt of this invention, respectively. The antibacterial film M1 which becomes the side which faces the skin at the time of use of the medical-application cladding material base S of the shape of a nonwoven fabric which consists of polymeric materials from at least one sort of matter among Ag, Au, Pt, Cu, Zn, Sn, and Ir is formed, the DLC film M4 is formed in the outside, and the medical-application cladding material shown in drawing (A) has these both mixolimnion m1' between the film M1 and Base S. The antibacterial film M1 has covered this medical-application cladding material to the some inside of the air hole (opening) S1 of not only the surface part of the medical-application cladding material base S but a base. On the other hand, the DLC film M4 of the outside is formed in the surface part of the antibacterial film M1, and is seldom formed to the hole S1. Therefore, the antibacterial film M1 is exposed partially and, thereby, antimicrobial activity is fully demonstrated. Moreover, since the DLC film M4 is formed in the surface part which touches the skin, it is hard to produce adhesion with a wound side. Moreover, of existence of mixolimnion m1', since it is good and the adhesion of the antibacterial film M1 and the DLC film M4 is also good, the adhesion of the film M1 and Base S is formed with adhesion sufficient on Base S as the whole film.

[0023] The adhesion layer M3 which becomes the side by which the medical-application cladding material shown in drawing (B) faces the skin at the time of use of Base S from at least one sort of matter among Ti, Cr, and Si is formed, the antibacterial film M1 which consists of at least one sort of matter among Ag, Au, Pt, Cu, Zn, Sn, and Ir is formed in the outside, and the DLC film M4 is further formed in the outside. The antibacterial film M1 has covered this medical-application cladding material to the some inside of the air hole (opening) S1 of not only the surface part of the medical-application cladding material base S but a base. On the other hand, the DLC film M4 of the outside is formed in the surface part of the antibacterial film M1, and is seldom formed to the hole S1. Therefore, the antibacterial film M1 is exposed partially and, thereby, antimicrobial activity is fully demonstrated. Moreover, since the DLC film M4 is formed in the surface part which touches the skin, it is hard to produce adhesion with a wound side. Moreover, to the both sides of Base S and the film M1, since adjustment is good and the adhesion of the antibacterial film M1 and the DLC film M4 also has it, the adhesion layer M3 is formed with adhesion sufficient on Base S as the whole film. [good]

[0024] The medical-application cladding material shown in drawing (C) to the side which faces the skin at the time of use of Base S Ti, The adhesion layer M3 which consists of at least one sort of matter among Cr and Si is formed. The barrier layer M2 which consists of Au, Pt, or Au and Pt is formed in the outside, the antibacterial film M1 which consists of at least one sort of matter among Ag, Pt, Cu, Zn, Sn, and Ir is formed in the outside, and the DLC film M4 is further formed in the outside. The antibacterial film M1 has covered this medical-application cladding material to the some inside of the air hole (opening) S1 of not only the surface part of the medical-application cladding material base S but a base. On the other hand, the DLC film M4 of the outside is formed in the surface part of the antibacterial film M1, and is seldom formed to the hole S1. Therefore, the antibacterial film M1 is exposed partially and, thereby, antimicrobial activity is fully demonstrated. Moreover, since the DLC film M4 is formed in the surface part which touches the skin, it is hard to produce adhesion with a wound side. moreover, some film M1 by oxygen being spread from the exterior through the film M1, and collecting on the interface part of the film M1 and a layer M3, or the constituent of the film M1 being spread into a layer M3 by existence of the barrier layer M2, -- exfoliation is controlled.

[0025] Moreover, in the medical-application cladding material of drawing (C), the antibacterial film M1, the barrier layer M2, and the adhesion layer M3 are formed by each by the ion vacuum evaporationo thin film forming method, and the medical-application cladding material shown in drawing (D) has mixolimnions m1, m2, and m3 between the lower layer, respectively. This medical-application cladding material has respectively the adhesion much more good by existence of mixolimnions m1, m2, and m3 between the adhesion layer M3 and the medical-application cladding material base S between the barrier layer M2 and the adhesion layer M3 between the antibacterial film M1 and the barrier layer M2.
[0026] In addition, in the medical-application cladding material of drawing (C), that in which the mixolimnion was formed only for one layer or two-layer by either is also considered. Moreover, also in the medical-application cladding material of drawing (B), what formed the antibacterial film M1 or (reaching) the adhesion layer M3 by the ion vacuum evaporationo thin film forming method can be considered. Moreover, drawing 2 is drawing showing the outline configuration of the membrane formation equipment which can be used for formation of the antibacterial film, a barrier layer, and an adhesion layer in manufacture of the medical-application cladding material concerning this invention, respectively. This equipment has a vacuum housing 1 and an evaporation source 3 and the ion source 4 are formed in the location which counters the holder 2 and holder 2 which support the formed membranes medical-application cladding material base S in a container 1. Moreover, in the holder 2 neighborhood, the thickness monitor 5 and the ion current measuring instrument 6 are arranged. Moreover, an exhauster 11 is attached to a container 1 and the inside of a container 1 can be made into a predetermined degree of vacuum.
[0027] Moreover, drawing 3 is membrane formation equipment by the plasma-CVD method which can be used for formation of the DLC film in manufacture of the medical-application cladding material concerning this invention. this equipment -- vacuum housing 1' -- having -- container 1' -- the gas nozzle 8 is installed in the location which counters inside at an electrode 7 and this. RF generator 72 is connected to an electrode 7, and container 1' is grounded. Moreover, the heater 71 for heating the goods S supported on it formed membranes to membrane formation temperature is attached to the electrode 7. container 1from stoma of a large number prepared in field which plasma material gas feed zone 9 is connected to gas nozzle 8, and counters electrode 7 ' -- plasma material gas can be introduced now inside. moreover, exhauster 11' attaches to container 1' -- having -- container 1' -- inside can be made into a predetermined degree of vacuum.
[0028] Next, the concrete example which manufactured the medical-application cladding material concerning this invention shown in said drawing 1 (D) is explained using the equipment of drawing 2 and drawing 3 . As a formed membranes medical-application cladding material base S, the nonwoven fabric which consists of polyethylene terephthalate was used. After cleaning a base S front face ultrasonically with an alcoholic system organic solvent in advance of film formation, it was made to dry for 30 minutes at 60 degrees C. Subsequently, the medical-application cladding material base S was carried in in the container 1 of the equipment of drawing 2 , and as film formation was carried out at the side to which reliance is divided into the skin at the time of use, after making a holder 2 support this base S, the inside of a container 1 was made into the degree of vacuum of 1x10 to 6 or less Torrs by operation of an exhauster 11.
[0029] Subsequently, from the ion source 4, Ar ion was irradiated with the acceleration voltage of 300V at Base S, and the base S front face was activated and cleaned. Then, evaporated Ti using the evaporation source 3, continuing Ar ion irradiation, it was made to vapor-deposit on the medical-application cladding material base S supported by the holder 2, and Ti adhesion layer M3 of 0.1 micrometers of thickness was formed on Base S. These both mixolimnion m3 was formed in the interface part of Base S and the adhesion layer M3 in connection with this.
[0030] Subsequently, vacuum evaporationo of Pt and the exposure of Ar ion as well as said Ti adhesion layer M3 formation were performed, and Pt barrier layer M2 of 0.1 micrometers of thickness was formed on Ti adhesion layer M3. These both mixolimnion m2 was formed in the interface part of the adhesion layer M3 and Pt barrier layer M2 in connection with this. Subsequently, vacuum evaporationo of Ag and the exposure of Ar ion were performed like said Ti adhesion layer M3 formation and said Pt

barrier layer M dimorphism **, and the Ag antibacterial film M1 of 0.4 micrometers of thickness was formed on Pt barrier layer M2. These both mixolimnion m1 was formed in the interface part of Pt barrier layer M2 and the Ag antibacterial film M1 in connection with this.
[0031] In addition, the degree of vacuum in a vacuum housing 1 was maintained at abbreviation 4x10-5Torr during membrane formation. Subsequently, the film covering base with which Ti adhesion layer M3, Pt barrier layer M2, and the Ag antibacterial film M1 were formed in the base S front face at this order container 1' of the equipment of drawing 3 -- it carried in inside, and the field in which said film was formed in this film covering base was turned to the direction of a gas nozzle 8, it installed on the electrode 7, and the inside of a container 1 was made into the degree of vacuum of 1x10 to 5 or less Torrs by operation of exhauster 11'.
[0032] subsequently, the stoma prepared in the gas nozzle 8 from the gas supply section 9 -- letting it pass -- container 1' -- methane (CH4) gas inside container 1' -- from a power source 72 the frequency of 13.56MHz to an electrode 7, while introducing until an inner degree of vacuum is set to 1x10-3Torr The high-frequency power of power 300W was supplied, this plasma-ized said introduced plasma material gas, and the DLC film M4 of 0.1 micrometers of thickness was formed in the outside of the Ag antibacterial film M1 of said film covering base under this plasma.
[0033] Thus, as shown in drawing 1 (D), the medical-application cladding material with which the adhesion layer M3, the barrier layer M2, the antibacterial film M3, and the DLC film M4 were formed at this order on the field which contacts the skin at the time of use of the medical-application cladding material base S was obtained. Next, film adhesion was evaluated, respectively about the medical-application cladding material obtained according to said this invention example, the medical-application cladding material (example 1 of a comparison) which used together Ag vacuum evaporationo and Ar ion irradiation, and formed Ag film on Base S, and the medical-application cladding material (example 2 of a comparison) which formed Ag film only by vacuum evaporationo on Base S. After evaluation of film adhesion having given the include angle of about 180 degrees and making it crooked 50 times, applying a steam to the film forming face of each medical-application cladding material, performing the tape friction test (it being used on the property of the configuration of a specimen article, without cutting) according to observing a membranous condition with the naked eye and X cut tape test (JIS K5400) estimated it. A result is shown in degree table 1.

表1

	膜の状態	Xカットテープ試験
実施例	剥離なし	剥離なし
比較例1	剥離なし	剥離なし
比較例2	剥離あり	全面剥離

Thus, it turns out that film adhesion even with after [good / the medical-application cladding material by the example 1 of a comparison which formed Ag film by each medical-application cladding material and the ion vacuum evaporationo thin film forming method by this invention example which formed each film (layer) by the ion vacuum evaporationo thin film forming method] 50 times crookedness is shown, and it can be equal to long duration use. It turns out that exfoliation has produced the medical-application cladding material by the example 2 of a comparison which does not use ion irradiation together and, on the other hand, does not have an adhesion layer and a barrier layer by being crooked 50 times, and it is hard to present practical use.
[0034] Next, the ease of removing of coagulation blood was evaluated, respectively about the medical-application cladding material and the unsettled medical-application cladding material base S which has not carried out film formation obtained by said this invention example and the example 1 of a comparison. About 0.1ml of Homo sapiens blood is dropped on the film of each film covering base, and it is 2 1cm. Extended and applied to the area range, where this spreading part is covered with a petri dish, put, and blood was made to solidify, the friction test was performed using adhesive tape about the clot-of-blood film, and the ease of removing of coagulation blood was investigated. A result is shown in

degree table 2.
表2

	凝固血液の剥がし易さ
実施例	容易に剥離
比較例1	一部残存
未処理基体	ほぼ全面残存

Thus, it is thought that the medical-application cladding material of this invention example can remove easily the blood solidified on the film, and can remove it from the exudate which adhered to this medical-application cladding material when it used for the wound side where blood etc. oozed out easily. On the other hand, with Ag film covering base of the example 1 of a comparison, it is thought that it is a little difficult to remove from an exudate, and it is thought with an unsettled base with it that it is very difficult to remove from an exudate.

[0035]

[Effect of the Invention] According to this invention, the medical-application cladding material which adhesion with a wound side cannot produce easily can be offered. Moreover, according to this invention, while having sufficient antimicrobial activity which can control growth of the bacteria in the wound section of the skin etc., this activity can be maintained and used over a long time, and the medical-application cladding material which adhesion with a wound side cannot produce easily can be offered further.

[Translation done.]

(19)日本国特許庁（ＪＰ）　(12)**公開特許公報**（Ａ）　(11)特許出願公開番号

特開平10－110257

(43)公開日　平成10年(1998)４月28日

(51)Int.Cl.[6]	識別記号	ＦＩ	
Ｃ２３Ｃ　14/06		Ｃ２３Ｃ　14/06	Ｆ
Ａ６１Ｌ　15/16		14/48	Ｄ
Ｃ２３Ｃ　14/48		Ａ６１Ｌ　15/01	

審査請求　未請求　請求項の数19　ＯＬ　（全７頁）

(21)出願番号　特願平8－262906

(22)出願日　平成８年(1996)10月３日

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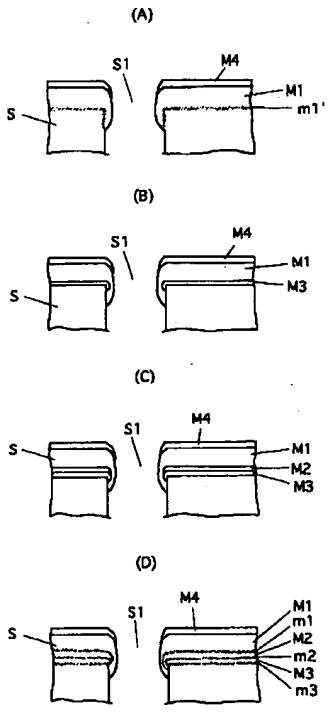
(54)【発明の名称】　医療用被覆材

(57)【要約】

【課題】創傷面との癒着が生じ難い医療用被覆材を提供する。

【解決手段】医療用被覆材の基体Ｓの皮膚に当てがわれる面側に抗菌活性を有する金属からなる抗菌性膜Ｍ１が形成され、抗菌性膜Ｍ１の外側に、抗菌性膜Ｍ１が部分的に露出する状態でダイヤモンド状炭素（ＤＬＣ）膜Ｍ４が形成されている医療用被覆材。



【特許請求の範囲】

【請求項１】　医療用被覆材基体の皮膚に当てがわれる面側に、抗菌活性を有する金属からなる抗菌性膜が形成され、該抗菌性膜の外側に該抗菌性膜が部分的に露出する状態でダイヤモンド状炭素（ＤＬＣ）膜が形成されていることを特徴とする医療用被覆材。

【請求項２】　前記抗菌性膜が蒸着とイオン照射を併用するイオン蒸着薄膜形成法により形成されたものである請求項１記載の医療用被覆材。

【請求項３】　前記抗菌性膜が銀（Ａｇ）、金（Ａｕ）、白金（Ｐｔ）、銅（Ｃｕ）、亜鉛（Ｚｎ）、スズ（Ｓｎ）及びイリジウム（Ｉｒ）のうち少なくとも１種の物質からなっている請求項１又は２記載の医療用被覆材。

【請求項４】　前記基体が通気性多孔質基体であり、前記抗菌性膜の膜厚が０．５μｍ以上５μｍ以下である請求項１、２又は３記載の医療用被覆材。

【請求項５】　前記ＤＬＣ膜の膜厚が０．０５μｍ以上０．５μｍ以下である請求項４記載の医療用被覆材。

【請求項６】　前記ＤＬＣ膜がプラズマＣＶＤ法により形成されたものである請求項１から５のいずれかに記載の医療用被覆材。

【請求項７】　前記医療用被覆材の基体が高分子材料からなるものである請求項１から６のいずれかに記載の医療用被覆材。

【請求項８】　医療用被覆材基体の皮膚に当てがわれる面側に、チタン（Ｔｉ）、クロム（Ｃｒ）及びシリコン（Ｓｉ）から選ばれた少なくとも１種の物質からなる密着層が形成され、該密着層の外側に銀（Ａｇ）、金（Ａｕ）、白金（Ｐｔ）、銅（Ｃｕ）、亜鉛（Ｚｎ）、スズ（Ｓｎ）及びイリジウム（Ｉｒ）から選ばれた少なくとも１種の物質からなる抗菌性膜が形成され、該密着層の外側に該抗菌性膜が部分的に露出する状態でダイヤモンド状炭素（ＤＬＣ）膜が形成されたことを特徴とする医療用被覆材。

【請求項９】　前記密着層及び前記抗菌性膜のうち少なくとも一方が、蒸着とイオン照射を併用するイオン蒸着薄膜形成法により形成されたものである請求項８記載の医療用被覆材。

【請求項１０】　前記基体が通気性多孔質基体であり、前記抗菌性膜の膜厚が０．５μｍ以上５μｍ以下である請求項８又は９記載の医療用被覆材。

【請求項１１】　前記ＤＬＣ膜の膜厚が０．０５μｍ以上０．５μｍ以下である請求項１０記載の医療用被覆材。

【請求項１２】　前記ＤＬＣ膜がプラズマＣＶＤ法により形成されたものである請求項８から１１のいずれかに記載の医療用被覆材。

【請求項１３】　前記医療用被覆材の基体が高分子材料からなるものである請求項８から１２のいずれかに記載の医療用被覆材。

【請求項１４】　医療用被覆材基体の皮膚に当てがわれる面側に、チタン（Ｔｉ）、クロム（Ｃｒ）及びシリコン（Ｓｉ）から選ばれた少なくとも１種の物質からなる密着層が形成され、該密着層の外側に金（Ａｕ）又は白金（Ｐｔ）又は金と白金からなるバリア層が形成され、該バリア層の外側に、銀（Ａｇ）、白金（Ｐｔ）、銅（Ｃｕ）、亜鉛（Ｚｎ）、スズ（Ｓｎ）及びイリジウム（Ｉｒ）から選ばれた少なくとも１種の物質からなる抗菌性膜が形成され、該抗菌性膜の外側に該抗菌性膜が部分的に露出する状態でダイヤモンド状炭素（ＤＬＣ）膜が形成されたことを特徴とする医療用被覆材。

【請求項１５】　前記密着層、前記バリア層及び前記抗菌性膜のうち少なくとも１の膜（層）が、蒸着とイオン照射を併用するイオン蒸着薄膜形成法により形成されたものである請求項１４記載の医療用被覆材。

【請求項１６】　前記基体が通気性多孔質基体であり、前記抗菌性膜の膜厚が０．５μｍ以上５μｍ以下である請求項１４又は１５記載の医療用被覆材。

【請求項１７】　前記ＤＬＣ膜の膜厚が０．０５μｍ以上０．５μｍ以下である請求項１６記載の医療用被覆材。

【請求項１８】　前記ＤＬＣ膜がプラズマＣＶＤ法により形成されたものである請求項１４から１７のいずれかに記載の医療用被覆材。

【請求項１９】　前記医療用被覆材の基体が高分子材料からなるものである請求項１４から１８のいずれかに記載の医療用被覆材。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、医療用被覆材、特に創傷部、熱傷部等の皮膚欠損部位を保護するための医療用被覆材に関する。

【０００２】

【従来の技術】皮膚の創傷部、熱傷部等は、通常、該部位を保護するために、該部位を乾燥状態に保った状態で痂皮形成により治癒を行うための医療用被覆材（ドライドレッシング材）や、該部位を適度の湿潤状態に保ち表皮細胞の遊走を促進することにより治癒を行うための医療用被覆材（ウェットドレッシング材）等で覆われる。ウェットドレッシング材は、創傷の乾燥壊死が抑制されて治癒が速やかであるが、滲出液が該ウェットドレッシング材と創傷面との間に溜まり易く、該部分は細菌等が増殖し易い環境となる。

【０００３】これらの医療用被覆材については、創傷面での細菌の増殖を抑制するために、抗菌活性を有する物質を付与することが試みられている。医療用被覆材に付与する抗菌活性物質としては、安定性の観点から無機化合物が多用される。例えば、特開昭６４－１５０５４号公報によると、銀、銅、亜鉛等の抗菌性金属を担持した

ゼオライトを、シリコンゴムからなる医療用被覆材の表面或いは全体に含ませたものが開示されている。

【０００４】また、例えば特開平４－９０７６４号公報及び特開平４－２７２７６４号公報によると、それぞれ多孔質ポリオレフィン及び熱可塑性ポリウレタンエラストマーからなる膜状の医療用被覆材の一方の表面に親水性ポリマーを化学的に結合させ、さらに該ポリマー結合面に抗菌性金属を蒸着又はイオンビーム照射により、薄膜化しない程度に付着させたものが開示されている。

【０００５】また、医療用被覆材で創傷面を被覆する際、創傷面に抗菌剤を含有するクリーム剤を塗布して感染を予防することも行われている。

【０００６】

【発明が解決しようとする課題】しかしながら、前記のドライドレッシング材、ウェットドレッシング材のいずれも、創傷面との癒着が生じ易く、ドレッシング材交換時に苦痛を伴うという問題がある。また、前記の、抗菌性ゼオライトを医療用被覆材の表面に塗布したり、全体に含ませたりした医療用被覆材は、抗菌性ゼオライトの塗布や分散により基材の特性が劣化する場合があり、一般的にはあまり使用されていない。

【０００７】また、前記の抗菌性金属を蒸着等させた医療用被覆材では、基材の屈曲による金属膜の剥離を避けるため、薄膜化しない程度に金属を付与してはいるものの、なお基材との十分な密着性が得られず、使用中に金属の剥離が生じ易いため、長時間にわたり十分な抗菌活性を維持することが困難である。また、抗菌剤を含むクリーム剤を塗布する方法では、該クリーム剤の大部分が医療用被覆材に吸収されてしまい効率が悪く、また塗布する手間がかかる。

【０００８】そこで本発明は、創傷面との癒着が生じ難い医療用被覆材を提供することを課題とする。また本発明は、皮膚の創傷部等での細菌の増殖を抑制できるだけの十分な抗菌活性を有するとともに、該活性を長時間にわたり維持して使用することができ、さらに、創傷面との癒着が生じ難い医療用被覆材を提供することを課題とする。

【０００９】

【課題を解決するための手段】本発明の医療用被覆材は、医療用被覆材の基体の皮膚に当てがわれる面側に、抗菌活性を有する金属からなる抗菌性膜が被覆され、該抗菌性膜の外側に該抗菌性膜が部分的に露出する状態でダイヤモンド状炭素（ＤＬＣ）膜が形成されたものである。

【００１０】最外層のＤＬＣ膜は創傷面との癒着抑制に有効である。前記抗菌活性を有する金属としては、代表的には強い抗菌力を有するＡｇを挙げることができるが、この他Ａｕ、Ｐｔ、Ｉｒ等の貴金属やＣｕ、Ｚｎ、Ｓｎ等も用いることができる。前記抗菌性膜はこれらのうち少なくとも１種の物質で構成することができる。

【００１１】本発明の医療用被覆材基体の材料としては、医療用被覆材の材料として通常用いられている綿等の天然高分子材料、ポリエチレン、ポリエチレンテレフタレート等の合成高分子材料等を例示でき、特に限定されない。また、その態様は、不織布状、フィルム状、や織物を重ねた態様等を例示できる。代表的なものとして綿、ポリエチレン、ポリエチレンテレフタレート等の高分子材料からなる通気性多孔質の基体（例えば高分子材料からなる通気性多孔質の不織布やフィルム等）を挙げることができる。

【００１２】基体が通気性多孔質の基体（例えば、多孔質フィルムや不織布からな基体）の場合、前記抗菌性膜の膜厚は０．５μｍ以上５μｍ以下程度とすることが望ましい。これは、最外層にＤＬＣ膜を形成する関係上、医療用被覆材基体の表面のみならず基体の孔（開口部）内部まで抗菌性膜がまわり込むことが望ましいところ、膜厚が０．５μｍより小さいと、基体の孔（開口部）内部まで抗菌性膜がまわり込むことが難しく、十分な抗菌活性が得られない恐れがあるからである。また、５μｍより大きいと、膜にクラックが生じ易く、このクラックに沿って剥離が生じ易くなるからである。また、膜厚は、前記範囲内で膜の材質、医療用被覆材基体の材質、該基体の孔部（開口部）面積等に応じて適宜定める。例えば、該基体の開口部面積が小さい場合、すなわち表面が比較的密に詰まっている場合、各開口部の内周面や縁への膜形成により開口部面積が著しく減小すると、通気性が悪くなり実用上好ましくないため、開口部面積を著しく減小しない程度に膜厚を小さくすることが考えられる。このためにも５μｍ以下が望ましい。

【００１３】前記ＤＬＣ膜の膜厚は、０．０５μｍ以上（例えば０．１μｍ以上）０．５μｍ以下程度とすることが望ましい。これは、膜厚が０．０５μｍより小さいと、膜形成を均一に行うことが難しく、十分な創傷面との癒着防止効果が得られない恐れがあるからであり、０．５μｍより大きいと、前記の抗菌性膜が全面的にＤＬＣ膜で覆われてしまって抗菌性膜の抗菌活性が十分に発揮されない恐れがあるからである。

【００１４】本発明の医療用被覆材によると、皮膚と接する表面部分にＤＬＣ膜が形成されているため、創傷面と癒着し難く、医療用被覆材交換時の苦痛が少ないものとなる。また、該ＤＬＣ膜の内側には少なくとも１種の抗菌活性を有する金属からなる抗菌性膜が形成され、該膜はＤＬＣ膜に被覆されているものの部分的に露出しているので、例えば前記の通気性多孔質基体を採用する場合、該膜を該基体の孔（開口）内部まで形成することでＤＬＣ膜に覆われない部分を残しておくことができ、このような抗菌性膜露出部分と創傷面からの滲出液とが接触して該膜中の抗菌性金属がイオンとして滲出液中に溶出し、抗菌性膜の有する抗菌活性が十分に発揮される。

【００１５】本発明の医療用被覆材において、前記医療用被覆材基体と前記抗菌性膜との間に、Ｔｉ、Ｃｒ及びＳｉのうち少なくとも１種の物質からなる密着層を有することが考えられる。例えば、抗菌性膜がＡｇ膜の場合においてＴｉ密着層を採用することができる。これらの密着層材料はいずれも、高分子材料等の通常医療用被覆材の材料として採用される材料及び前記抗菌性膜材料の双方との整合性が比較的良く、該基体と抗菌性膜との密着性を高める役割をする。

【００１６】さらに、本発明の医療用被覆材において、前記密着層と前記抗菌性膜との間にＡｕ又はＰｔ又は該両者からなるバリア層を有し、前記抗菌性膜がＡｇ、Ｐｔ、Ｉｒ、Ｃｕ、Ｚｎ、Ｓｎのうち少なくとも１種の物質からなることが考えられる。例えば、抗菌性膜がＡｇ膜で密着層がＴｉ層の場合において、Ｐｔからなるバリア層を採用することができる。バリア層を有しない場合、抗菌性膜を通して酸素が拡散する恐れがあり、その場合該酸素が抗菌性膜と密着層との界面部分に達して該部分での抗菌性膜の剥離が生じ易くなる。また、バリア層を有しない場合、抗菌性膜構成物質が密着層内へ拡散し易く、その場合抗菌性膜が剥離し易くなるが、バリア層はこのような酸素又は（及び）抗菌性膜構成物質の拡散を抑制し、抗菌性膜の密着性を向上させることができる。

【００１７】本発明の医療用被覆材において、前記の密着層やバリア層を形成することなく基体上に直接抗菌性膜を形成する場合は該膜形成を、抗菌性膜及び密着層を有するときにはいずれか一方又は双方の膜（層）形成を、抗菌性膜、バリア層及び密着層を有するときには少なくとも１の膜（層）形成を、蒸着とイオン照射を併用するイオン蒸着薄膜形成法により行うことが考えられる。

【００１８】これにより、照射イオンの作用で、イオン照射面が活性化されるとともに、形成した膜（層）とその下層との間に該両者の混合層が形成されて、該膜（層）の密着性が向上する。照射イオンとしては、窒素イオン、水素イオン、不活性ガスイオン（ヘリウム（Ｈｅ）イオン、ネオン（Ｎｅ）イオン、アルゴン（Ａｒ）イオン、クリプトン（Ｋｒ）イオン、キセノン（Ｘｅ）イオン等）等を用いることができる。

【００１９】イオン照射時の加速電圧はイオン種、イオン照射面の材質等により異なるが、１００Ｖ以上２ｋＶ以下程度とすることが望ましい。これは、１００Ｖより小さいと、イオン照射の効果が照射面内で不均一になり、膜密着性が十分でない領域が生じる恐れがあるからであり、２ｋＶより大きいと、イオン照射に伴う熱の影響で医療用被覆材基体の劣化が生じる可能性が大きいからである。

【００２０】また、本発明の医療用被覆材において、医療用被覆材基体として、膜（層）形成前にイオン照射により表面をクリーニングしたものを用いることが考えられ、この場合、膜（層）密着性が一層優れたものとなる。このように、イオン蒸着薄膜形成法を採用することで、形成膜（層）が基体の屈曲によっても従来の膜より剥離し難いものとなり、このような被覆材は抗菌活性を維持したまま長時間使用できる。

【００２１】また、本発明の医療用被覆材において、前記ＤＬＣ膜はその形成方法は特に限定されないが、代表的にはプラズマＣＶＤ法により形成されたものを例示できる。なお、本発明の医療用被覆材は、前記ＤＬＣ膜とその内側の膜（層）との密着性も良いことから膜全体として基体上に密着性良好に形成されている。

【００２２】

【発明の実施の形態】以下、本発明の実施の形態を図面を参照して説明する。図１（Ａ）、（Ｂ）、（Ｃ）及び（Ｄ）はそれぞれ本発明の実施形態である医療用被覆材の一部の拡大断面図である。図（Ａ）に示す医療用被覆材は高分子材料からなる不織布状の医療用被覆材基体Ｓの、使用時に皮膚に面する側にＡｇ、Ａｕ、Ｐｔ、Ｃｕ、Ｚｎ、Ｓｎ及びＩｒのうち少なくとも１種の物質からなる抗菌性膜Ｍ１が形成され、その外側にＤＬＣ膜Ｍ４が形成され、膜Ｍ１と基体Ｓとの間に該両者の混合層ｍ１´を有するものである。この医療用被覆材は、抗菌性膜Ｍ１が医療用被覆材基体Ｓの表面部分のみならず基体の通気孔（開口）Ｓ１の若干内側までも覆っている。一方、その外側のＤＬＣ膜Ｍ４は抗菌性膜Ｍ１の表面部分に形成され、孔Ｓ１まではあまり形成されていない。従って、抗菌性膜Ｍ１は部分的に露出しており、これにより抗菌活性は十分に発揮される。また、皮膚と接する表面部分にはＤＬＣ膜Ｍ４が形成されているため創傷面との癒着が生じ難い。また、混合層ｍ１´の存在により膜Ｍ１と基体Ｓとの密着性は良好であり、抗菌性膜Ｍ１とＤＬＣ膜Ｍ４との密着性も良好であることから、膜全体として基体Ｓ上に密着性良く形成されている。

【００２３】図（Ｂ）に示す医療用被覆材は、基体Ｓの、使用時に皮膚に面する側にＴｉ、Ｃｒ及びＳｉのうち少なくとも１種の物質からなる密着層Ｍ３が形成され、その外側にＡｇ、Ａｕ、Ｐｔ、Ｃｕ、Ｚｎ、Ｓｎ及びＩｒのうち少なくとも１種の物質からなる抗菌性膜Ｍ１が形成され、さらにその外側にＤＬＣ膜Ｍ４が形成されたものである。この医療用被覆材は、抗菌性膜Ｍ１が医療用被覆材基体Ｓの表面部分のみならず基体の通気孔（開口）Ｓ１の若干内側までも覆っている。一方、その外側のＤＬＣ膜Ｍ４は抗菌性膜Ｍ１の表面部分に形成され、孔Ｓ１まではあまり形成されていない。従って、抗菌性膜Ｍ１は部分的に露出しており、これにより抗菌活性は十分に発揮される。また、皮膚と接する表面部分にはＤＬＣ膜Ｍ４が形成されているため創傷面との癒着が生じ難い。また、密着層Ｍ３が基体Ｓと膜Ｍ１の双方に対し整合性がよく、抗菌性膜Ｍ１とＤＬＣ膜Ｍ４との密

着性も良好であることから、膜全体として基体Ｓ上に密着性良く形成されている。

【００２４】図（Ｃ）に示す医療用被覆材は、基体Ｓの、使用時に皮膚に面する側にＴｉ、Ｃｒ及びＳｉのうち少なくとも１種の物質からなる密着層Ｍ３が形成され、その外側にＡｕ、Ｐｔ又はＡｕ及びＰｔからなるバリア層Ｍ２が形成され、その外側にＡｇ、Ｐｔ、Ｃｕ、Ｚｎ、Ｓｎ及びＩｒのうち少なくとも１種の物質からなる抗菌性膜Ｍ１が形成され、さらにその外側にＤＬＣ膜Ｍ４が形成されたものである。この医療用被覆材は、抗菌性膜Ｍ１が医療用被覆材基体Ｓの表面部分のみならず基体の通気孔（開口）Ｓ１の若干内側までも覆っている。一方、その外側のＤＬＣ膜Ｍ４は抗菌性膜Ｍ１の表面部分に形成され、孔Ｓ１まではあまり形成されていない。従って、抗菌性膜Ｍ１は部分的に露出しており、これにより抗菌活性は十分に発揮される。また、皮膚と接する表面部分にはＤＬＣ膜Ｍ４が形成されているため創傷面との癒着が生じ難い。また、バリア層Ｍ２の存在により、膜Ｍ１を介して外部から酸素が拡散して膜Ｍ１と層Ｍ３との界面部分に溜まったり、膜Ｍ１の構成成分が層Ｍ３内へ拡散したりすることによる膜Ｍ１の一部剥離が抑制されている。

【００２５】また、図（Ｄ）に示す医療用被覆材は、図（Ｃ）の医療用被覆材において、抗菌性膜Ｍ１、バリア層Ｍ２、密着層Ｍ３がいずれもイオン蒸着薄膜形成法により形成されたものであり、それぞれその下層との間に混合層ｍ１、ｍ２、ｍ３を有している。この医療用被覆材は、混合層ｍ１、ｍ２、ｍ３の存在により、抗菌性膜Ｍ１とバリア層Ｍ２との間、バリア層Ｍ２と密着層Ｍ３との間、密着層Ｍ３と医療用被覆材基体Ｓとの間の密着性がそれぞれ一層良好なものである。

【００２６】なお、図（Ｃ）の医療用被覆材において、混合層がいずれかに１層又は２層のみ形成されたものも考えられる。また、図（Ｂ）の医療用被覆材においても、抗菌性膜Ｍ１又は（及び）密着層Ｍ３をイオン蒸着薄膜形成法により形成したものが考えられる。また、図２は本発明に係る医療用被覆材の製造において抗菌性膜、バリア層及び密着層の形成にそれぞれ用いることができる成膜装置の概略構成を示す図である。この装置は真空容器１を有し、容器１内には被成膜医療用被覆材基体Ｓを支持するホルダ２及びホルダ２に対向する位置に蒸発源３及びイオン源４が設けられている。また、ホルダ２付近には膜厚モニタ５及びイオン電流測定器６が配置されている。また、容器１には排気装置１１が付設されて容器１内を所定の真空度にすることができる。

【００２７】また、図３は本発明に係る医療用被覆材の製造においてＤＬＣ膜の形成に用いることができるプラズマＣＶＤ法による成膜装置である。この装置は、真空容器１´を有し、容器１´内には電極７及びこれに対向する位置にガスノズル８が設置されている。電極７には高周波電源７２が接続され、容器１´は接地されている。また、電極７にはその上に支持される被成膜物品Ｓを成膜温度に加熱するためのヒータ７１が付設されている。ガスノズル８にはプラズマ原料ガス供給部９が接続されており、電極７に対向する面に設けられた多数の小孔から容器１´内にプラズマ原料ガスを導入できるようになっている。また、容器１´には排気装置１１´が付設されて容器１´内を所定の真空度にすることができる。

【００２８】次に、図２及び図３の装置を用いて、本発明に係る、前記図１（Ｄ）に示す医療用被覆材を製造した具体的実施例について説明する。被成膜医療用被覆材基体Ｓとして、ポリエチレンテレフタレートからなる不織布を用いた。膜形成に先立ち、基体Ｓ表面を、アルコール系有機溶媒で超音波洗浄した後、６０℃で３０分間乾燥させた。次いで、図２の装置の容器１内に医療用被覆材基体Ｓを搬入し、該基体Ｓを使用時に皮膚に当てがわれる側に膜形成されるようにして、ホルダ２に支持させた後、排気装置１１の運転にて容器１内を1×10^{-6}Ｔｏｒｒ以下の真空度とした。

【００２９】次いで、イオン源４からＡｒイオンを３００Ｖの加速電圧で基体Ｓに照射し、基体Ｓ表面を活性化及びクリーニングした。その後、Ａｒイオン照射を継続しながら蒸発源３を用いてＴｉを蒸発させ、ホルダ２に支持された医療用被覆材基体Ｓ上に蒸着させて、基体Ｓ上に層厚０．１μｍのＴｉ密着層Ｍ３を形成した。これに伴い、基体Ｓと密着層Ｍ３との界面部分に該両者の混合層ｍ３が形成された。

【００３０】次いで、前記Ｔｉ密着層Ｍ３形成と同様にしてＰｔの蒸着とＡｒイオンの照射を行い、Ｔｉ密着層Ｍ３上に層厚０．１μｍのＰｔバリア層Ｍ２を形成した。これに伴い、密着層Ｍ３とＰｔバリア層Ｍ２との界面部分に該両者の混合層ｍ２が形成された。次いで、前記Ｔｉ密着層Ｍ３形成及び前記Ｐｔバリア層Ｍ２形成と同様にしてＡｇの蒸着とＡｒイオンの照射を行い、Ｐｔバリア層Ｍ２上に膜厚０．４μｍのＡｇ抗菌性膜Ｍ１を形成した。これに伴い、Ｐｔバリア層Ｍ２とＡｇ抗菌性膜Ｍ１との界面部分に該両者の混合層ｍ１が形成された。

【００３１】なお、成膜中は真空容器１内の真空度を約4×10^{-5}Ｔｏｒｒに保った。次いで、基体Ｓ表面にＴｉ密着層Ｍ３、Ｐｔバリア層Ｍ２及びＡｇ抗菌性膜Ｍ１がこの順に形成された膜被覆基体を、図３の装置の容器１´内に搬入し、該膜被覆基体を前記膜が形成された面をガスノズル８の方に向けて電極７上に設置し、排気装置１１´の運転にて容器１内を1×10^{-5}Ｔｏｒｒ以下の真空度とした。

【００３２】次いで、ガス供給部９からガスノズル８に設けられた小孔を通して容器１´内にメタン（CH_4）ガスを、容器１´内の真空度が1×10^{-3}Ｔｏｒｒにな

るまで導入するとともに電極７に電源７２から周波数１３．５６ＭＨｚ、電力３００Ｗの高周波電力を供給し、これにより前記導入したプラズマ原料ガスをプラズマ化し、該プラズマの下で前記膜被覆基体のＡｇ抗菌性膜Ｍ１の外側に膜厚０．１μｍのＤＬＣ膜Ｍ４を形成した。

【００３３】このようにして、図１（Ｄ）に示すように、医療用被覆材基体Ｓの、使用時に皮膚と接触する面上に密着層Ｍ３、バリア層Ｍ２、抗菌性膜Ｍ３及びＤＬＣ膜Ｍ４がこの順に形成された医療用被覆材を得た。次に、前記本発明実施例により得られた医療用被覆材、基体Ｓ上にＡｇ蒸着とＡｒイオン照射を併用してＡｇ膜を形成した医療用被覆材（比較例１）、及び基体Ｓ上に蒸着のみによりＡｇ膜を形成した医療用被覆材（比較例２）について、それぞれ膜密着性を評価した。膜密着性の評価は、各医療用被覆材の膜形成面に水蒸気を当てながら、約１８０度の角度をつけて５０回屈曲させた後、膜の状態を肉眼で観察すること及びＸカットテープ試験（ＪＩＳ　Ｋ５４００）に準じたテープ剥離試験（被検物品の形状の特性上、カットせずに使用）を行うことで評価した。結果を次表１に示す。

表１

	膜の状態	Ｘカットテープ試験
実施例	剥離なし	剥離なし
比較例１	剥離なし	剥離なし
比較例２	剥離あり	全面剥離

このように、イオン蒸着薄膜形成法により各膜（層）を形成した本発明実施例による各医療用被覆材及びイオン蒸着薄膜形成法によりＡｇ膜を形成した比較例１による医療用被覆材は、５０回屈曲後も良好な膜密着性を示し、長時間使用に耐え得ることが分かる。一方、イオン照射を併用せず、また密着層及びバリア層を有しない比較例２による医療用被覆材は、５０回屈曲することにより、剥離が生じており、実用に供し難いことが分かる。

【００３４】次に、前記本発明実施例、比較例１により得られた医療用被覆材及び膜形成していない未処理の医療用被覆材基体Ｓについて、それぞれ凝固血液の剥がし易さを評価した。各膜被覆基体の膜上にヒト血液約０．１ｍｌを滴下して１ｃｍ^{2}の面積範囲に広げて塗布し、該塗布部分をシャーレで覆った状態で静置して血液を凝固させ、凝血膜について粘着テープを用いて剥離試験を行い、凝固血液の剥がし易さを調べた。結果を次表２に示す。

表２

	凝固血液の剥がし易さ
実施例	容易に剥離
比較例１	一部残存
未処理基体	ほぼ全面残存

このように、本発明実施例の医療用被覆材は、膜上で凝固した血液を容易に剥がすことができ、血液等が滲出した創傷面に用いた場合に該医療用被覆材と癒着した滲出液から容易に剥がすことができると考えられる。一方、比較例１のＡｇ膜被覆基体では、滲出液から剥がすことがやや難しいと考えられ、未処理の基体では滲出液から剥がすことが非常に難しいと考えられる。

【００３５】

【発明の効果】本発明によると、創傷面との癒着が生じ難い医療用被覆材を提供することができる。また本発明によると、皮膚の創傷部等での細菌の増殖を抑制できるだけの十分な抗菌活性を有するとともに、該活性を長時間にわたり維持して使用することができ、さらに、創傷面との癒着が生じ難い医療用被覆材を提供することができる。

【図面の簡単な説明】

【図１】図（Ａ）、（Ｂ）、（Ｃ）及び（Ｄ）は、それぞれ本発明の実施形態である医療用被覆材の一部の拡大断面図である。

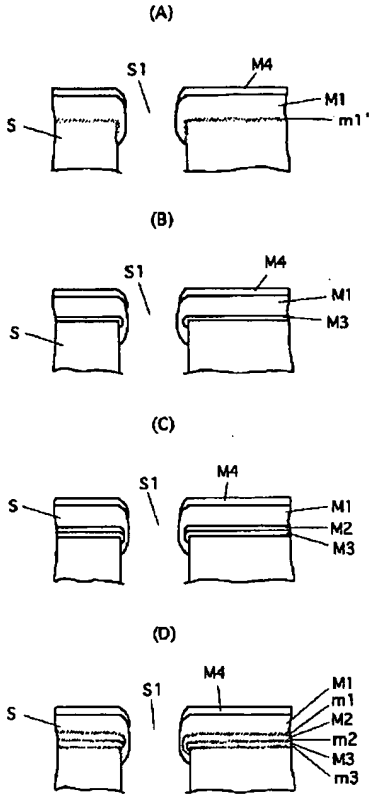
【図２】本発明に係る医療用被覆材の製造において、密着層、バリア層及び抗菌性膜の形成にそれぞれ用いることができる成膜装置の概略構成を示す図である。

【図３】本発明に係る医療用被覆材の製造において、ＤＬＣ膜の形成に用いることができる成膜装置の概略構成を示す図である。

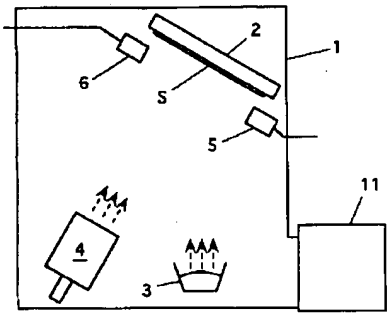
【符号の説明】

１、１´　真空容器
１１、１１´　排気装置
２　被成膜物品支持ホルダ
３　蒸発源
４　イオン源
５　膜厚モニタ
６　イオン電流測定器
７　高周波電極
７１　ヒータ
７２　高周波電源
８　ガスノズル
９　プラズマ原料ガス供給部
Ｓ　医療用被覆材基体
Ｍ１　抗菌性膜
Ｍ２　バリア層
Ｍ３　密着層
Ｍ４　ＤＬＣ膜
ｍ１、ｍ１´、ｍ２、ｍ３　混合層

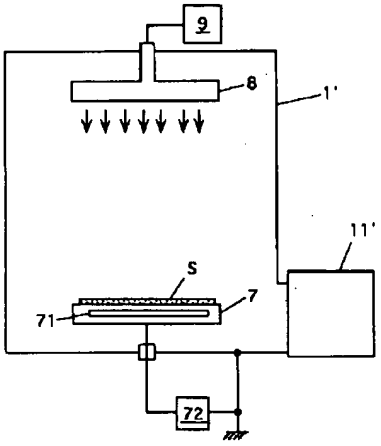
【図１】


(A)
S1
M4
S
M1
m1'
(B)
S1
M4
S
M1
M3
(C)
S
S1
M4
M1
M2
M3
(D)
S
S1
M4
M1
m1
M2
m2
M3
m3

【図２】


2
1
6
S
5
11
4
3

【図３】


9
8
1'
11'
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7
71
72

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